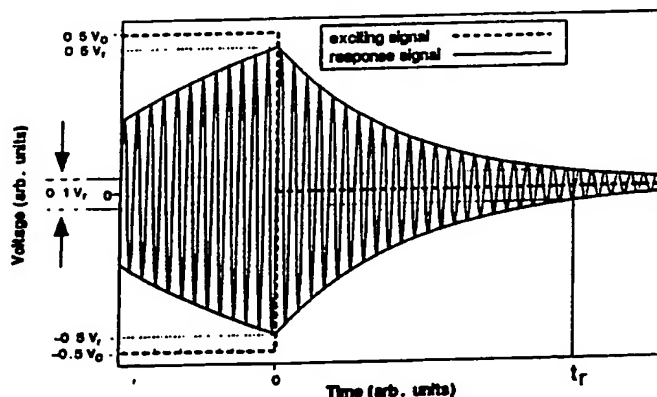




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : H01F 1/153, G08G 13/24	A1	(11) International Publication Number: WO 90/03652 (43) International Publication Date: 5 April 1990 (05.04.90)
(21) International Application Number: PCT/US89/03513 (22) International Filing Date: 16 August 1989 (16.08.89) (30) Priority data: 248,699 26 September 1988 (26.09.88) US (71) Applicant: ALLIED-SIGNAL INC. [US/US]; Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07960 (US). (72) Inventor: RAMANAN, V., R., V. ; 111 Richard Street, Dover, Morris County, NJ 07801 (US). (74) Agent: WINTER, Richard, C.; Allied-Signal Inc., Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07960 (US).		(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK, FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>

(54) Title: METALLIC GLASS ALLOYS FOR MECHANICALLY RESONANT TARGET SURVEILLANCE SYSTEMS



(57) Abstract

A magnetic metallic glass alloy evidencing a low rate of damping of mechanically resonant oscillations, is suitable for use in mechanically resonant target surveillance systems. The alloy has a composition described by the formula $Fe_aNi_bM_cB_dSi_eCr_f$, where M is one of molybdenum and chromium, "a"-"f" are in atom percent, "a" ranges from about 39 to about 41, "b" ranges from about 37 to about 39, "c" ranges from 0 to about 3, "d" ranges from about 17 to about 19, and "e" and "f" range from 0 to about 2, with the provisos that (i) only one of "c", "e", and "f" can be zero, (ii) "e" cannot be zero if "f" is not zero, and (iii) "f" can be zero only when M is Cr. A ribbon, wire or sheet of this alloy, having mechanical resonance in a range of frequencies from about 55 kHz to about 60 kHz, evidences a ring down time of at least about 3 ms.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MR	Mauritania
BE	Belgium	GA	Gabon	MW	Malawi
BF	Burkina Faso	GB	United Kingdom	NL	Netherlands
BG	Bulgaria	HU	Hungary	NO	Norway
BJ	Benin	IT	Italy	RO	Romania
BR	Brazil	JP	Japan	SD	Sudan
CA	Canada	KP	Democratic People's Republic of Korea	SE	Sweden
CF	Central African Republic	KR	Republic of Korea	SN	Senegal
CG	Congo	LI	Liechtenstein	SU	Soviet Union
CH	Switzerland	LK	Sri Lanka	TD	Chad
CM	Cameroon	LU	Luxembourg	TG	Togo
DE	Germany, Federal Republic of	MC	Monaco	US	United States of America
DK	Denmark				

METALLIC GLASS ALLOYS FOR MECHANICALLY
RESONANT TARGET SURVEILLANCE SYSTEMS

BACKGROUND OF THE INVENTION

5

1. Field of the Invention

This invention relates to metallic glass alloys;
and more particularly to metallic glass alloys suited
for use in mechanically resonant targets of article
10 surveillance systems.

2. Description of the prior art

Numerous article surveillance systems are available
in the market today to help identify and/or secure
15 various animate and inanimate objects. Identification
of personnel for controlled access to limited areas, and
securing articles of merchandise against pilferage are
examples of purposes for which such systems are
employed.

20 An essential component of all surveillance systems
is a sensing unit, or "target", that is attached to the
object to be detected. Other components of the system
include a transmitter and a receiver that are suitably
disposed in an "interrogation" zone. When the object
25 carrying the target enters the interrogation zone, the
functional part of the target responds to a signal from
the transmitter, which response is detected in the
receiver. The information contained in the response
signal is then processed for actions appropriate to the
30 application: denial of access, triggering of an alarm,
and the like.

Surveillance systems that employ detection modes
incorporating the fundamental mechanical resonance
frequency of the target material are especially
35 advantageous systems, in that they offer a combination
of high detection sensitivity, high operating
reliability, and low operating costs. Examples of such

systems are disclosed in U.S. Patent Nos. 4,510,489 and 4,510,490 (hereinafter the '489 and '490 patents).

The target in such systems is a strip, or a plurality of strips, of known length of a ferromagnetic material, packaged with a harder ferromagnet (material with a higher coercivity) that provides a biasing field to establish peak magnetomechanical coupling. The ferromagnetic material is preferably a metallic glass alloy ribbon, since the efficiency of magnetomechanical coupling in these alloys is very high. The mechanical resonance frequency of the target material is dictated essentially by the length of the alloy ribbon and the biasing field strength. When an interrogating signal tuned to this resonance frequency is encountered, the target material responds with a large signal field which is detected by the receiver. The large signal field is attributable to an enhanced magnetic permeability of the target material at the resonance frequency. Various target configurations and systems for interrogation and detection that utilize the above principle have been taught in the '489 and '490 patents.

In one particularly useful system, the target material is excited into oscillations by pulses, or bursts, of signal at its resonance frequency generated by the transmitter. When the exciting pulse is over, the target material will undergo damped oscillations at its resonance frequency, i.e., the target material "rings down" following the termination of the exciting pulse. The receiver "listens" to the response signal during this ring down period. Under this arrangement, the surveillance system is relatively immune to interferences from various radiated or power line conducted sources and, therefore, the potential for false alarms is essentially eliminated.

A broad range of alloys have been claimed in the '489 and '490 patents as suitable for target material, for the various detection systems disclosed. Other metallic glass alloys bearing high permeabilities are

disclosed in U.S. Patent No. 4,152,144; the compositions of the alloys claimed in this patent fall within the broad range referred to above.

However, for the particular detection system described immediately above, metallic glass alloys with long ring down times are highly desirable so that detection efficiencies in the system may be improved. Of these, glassy metal alloys that are economical to produce would offer an additional advantage.

10

SUMMARY OF THE INVENTION

The present invention provides magnetic alloys that are at least about 70% glassy and are characterized by long ring down times in resonance target applications. Such alloys evidence a low rate of damping of resonant oscillations, following the termination of an exciting pulse. Generally stated, the glassy metal alloys of the invention have a composition described by the formula $Fe_aNi_bM_cB_dSi_eCr_f$, where M is one of molybdenum and chromium, "a" - "f" are in atom percent, "a" ranges from about 39 to about 41, "b" ranges from about 37 to about 39, "c" ranges from 0 to about 3, "d" ranges from about 17 to about 19, and "e" and "f" range from 0 to about 2, with the provisos that (i) only one of "c", "e" and "f" can be zero, (ii) "e" cannot be zero if "f" is not zero, and (iii) "f" can be zero only when M is Cr. Ribbons of these alloys, when mechanically resonant at frequencies ranging from about 55 kHz to about 60 kHz, evidence ring down times of at least about 3 ms. Alternatively, ribbons of these alloys, when mechanically resonant at frequencies ranging from about 21 kHz to about 25 kHz, evidence ring down times of at least about 7 ms.

The metallic glasses of this invention are especially suitable for use as the active elements in targets associated with surveillance systems that employ resonance frequency excitation and detection modes. Other uses may be found in special magnetic amplifiers, relay cores, ground fault interrupters and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be more fully understood and further advantages will become apparent when reference is made to the following detailed description of the preferred embodiments of the invention and the accompanying drawing, which is a schematic representation of the exciting signal pulse and the resultant response signal of the target material, the envelopes of these signals being indicated by the thick dashed and thick continuous lines respectively, and wherein the definitions of the peak response voltage, V_r , and the ring down time, t_r , of the target material are also provided.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, there are provided magnetic metallic glass alloys that are characterized by long ring down times in resonance target applications. These alloys evidence a low rate of damping of resonant oscillations, following the termination of an exciting pulse. Generally stated, the glassy metal alloys of the invention have a composition described by the formula $Fe_aNi_bM_cB_dSi_eC_f$, where M is one of molybdenum and chromium, "a" - "f" are in atom percent, "a" ranges from about 39 to about 41, "b" ranges from about 37 to about 39, "c" ranges from 0 to about 3, "d" ranges from about 17 to about 19, and "e" and "f" range from 0 to about 2, with the provisos that (i) only one of "c", "e" and "f" can be zero, (ii) "e" cannot be zero if "f" is not zero, and (iii) "f" can be zero only when M is Cr. The purity of the above compositions is that found in normal commercial practice. Ribbons of these alloys, at lengths ranging from about 35 mm to about 40 mm exhibit mechanical resonance in a range of frequencies from about 55 kHz to about 60 kHz. When thus resonant, such ribbons evidence ring down times of at least about 3 ms. Alternatively,

ribbons of these alloys, at lengths ranging from about 85 mm to about 100 mm exhibit mechanical resonance in a range of frequencies from about 21 kHz to about 25 kHz; and, when so resonant, evidence ring down times of at least about 7 ms.

Ribbons having mechanical resonances in the range from about 55 kHz to about 60 kHz are preferred. Such ribbons are short enough to be used as disposable target materials. In addition, the resonance signals of such ribbons are well separated from the audio and commercial radio frequency ranges.

Most metallic glass alloys that are outside of the scope of this invention typically ring down, after excitation of a resonance in a frequency range from about 55 kHz to about 60 kHz, in times shorter than about 2 ms. These ring down times are unacceptable because of the increased difficulties associated with the detection of a response signal of reasonable strength within such short time intervals.

There are a few metallic glass alloys outside of the scope of this invention that do show ring down times comparable to those from the alloys of this invention. However, these alloys invariably contain high levels of molybdenum. Aside from the increased raw material costs associated with Mo, the yield of good magnetic ribbon, suitable for use in resonance targets, from casts of alloys with high Mo content tends to be generally poor. The alloys of the present invention offer the advantageous combination of long ring down times and economy in production of usable ribbon.

Apart from the ease in detection facilitated by the longer ring down times in the alloys of this invention, such longer time intervals provide an additional, and advantageous, feature in the detection system in that the receiver may "listen" to the sample response more than once during the same ring down cycle, for confirmation purposes.

Examples of metallic glasses of the invention include $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_2\text{B}_{18}\text{Si}_1\text{C}_1$, $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_3\text{B}_{18}\text{Si}_{0.5}\text{Co}_{0.5}$, $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_1\text{B}_{18}\text{Si}_{1.5}\text{C}_{1.5}$, $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_{2.5}\text{B}_{17.5}\text{Si}_1\text{C}_1$, $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_{1.5}\text{B}_{18.5}\text{Si}_1\text{C}_1$, $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_3\text{B}_{17}\text{Si}_1\text{C}_1$,
5 $\text{Fe}_{40}\text{Ni}_{38}\text{Cr}_2\text{B}_{18}\text{Si}_2$, and $\text{Fe}_{40}\text{Ni}_{38}\text{B}_{18}\text{Si}_2\text{C}_2$, where all numbers are in atomic percent.

The definition of the ring down time, as used in the context of the description of this invention, is provided in the Figure. This Figure also illustrates,
10 schematically, the interrogation and detection modes of a surveillance system wherein the alloys of this invention are beneficially employed.

The target material is exposed to a burst of exciting signal of constant amplitude, referred to as
15 the exciting pulse, tuned to the frequency of mechanical resonance of the target material. The exciting pulse is outlined in thick dashed lines in the Figure, and the peak-to-peak amplitude of the pulse is denoted by the quantity V_0 . Although the principle of operation of the
20 surveillance system is not dependent on the shape of the waves comprising the exciting pulse, the wave form of this signal is usually sinusoidal. The target material begins to resonate under this excitation.

The physical principle governing this resonance may
25 be summarized as follows: When a ferromagnetic material is subjected to a magnetizing magnetic field, it experiences a change in length. The fractional change in length, over the original length, of the material is referred to as magnetostriction and denoted by the
30 symbol λ . A positive signature is assigned to λ if an elongation occurs parallel to the magnetizing magnetic field.

When a ribbon of a material with a positive magnetostriction is subjected to a sinusoidally varying
35 external field, applied along its length, the ribbon will undergo periodic changes in length, i.e., the ribbon will be driven into oscillations. The external field may be generated, for example, by a solenoid

carrying a sinusoidally varying current. The frequency of the ribbon oscillations will be twice that of the driving field, since the magnetostriction is insensitive to the direction of the driving field at any given instant. In other words, as long as the absolute magnitude of the driving field is non-zero, there will be a change in the ribbon length. Magnetomechanical resonance occurs when the frequency of the driving field is one-half of f_r , the mechanical resonance frequency of the ribbon. The frequency f_r is given by the relation

$$f_r = (1/2L)(E/D)^{0.5},$$

where L is the ribbon length, E is the Young's modulus of the ribbon, and D is the density of the ribbon.

However, if a dc magnetic field, referred to as the biasing field, of suitable strength were imposed on the material concurrently with the ac field, the frequency of ribbon oscillations will be that of the driving ac field. The reason for this is that the material responds magnetostrictively to the net instantaneous magnetic field acting upon it, and as long as this net field stays non-zero, the material will oscillate about the position where the constant dc field has placed it. Apart from providing a sensitivity to the direction of the instantaneous ac field, the biasing field serves other purposes as well.

Magnetostrictive effects are observed in a ferromagnetic material only when the magnetization of the material proceeds through domain rotation. No magnetostriction is observed when motion of plane parallel domain walls is the mechanism for magnetization. The biasing field places the material at, or beyond, the "knee" of hysteresis loop of the material, in which magnetic state the motion of plane parallel walls has been expended, and further magnetization of the sample occurs mainly by domain rotation. The efficiency of magnetomechanical response from the material has thus been improved. It is also well understood in the art that a biasing field serves

to change the effective value for E in a ferromagnetic material so that the mechanical resonance frequency of the material may be modified by a suitable choice of strength for the biasing field.

5 Summarizing the above, a ribbon of a positively magnetostrictive ferromagnetic material, when exposed to a driving ac magnetic field in the presence of a dc
10 biasing field, will oscillate at the frequency of the driving ac field, and when this frequency coincides with the mechanical resonance frequency, f_r , of the material, the ribbon will resonate and provide increased response
15 signal amplitudes. In practice, the biasing field is provided by a ferromagnet with a higher coercivity than the target material present in the "target package".

15 The amplitude of the response signal, or voltage, from the target material increases through the duration of the exciting pulse (as dictated by inertia), and eventually reaches a stable, constant value if the
20 exciting pulse lasts for a long enough time. The peak-to-peak height of this stable amplitude is represented as V_r in the Figure. Once the exciting pulse is turned off, the target material "rings down", i.e., the
25 amplitude of mechanical oscillations in the material and, consequently, the response voltage amplitude reduce to zero over a period of time. In other words, in the
30 absence of an excitation, the motion of the excited target material is damped. The profile of the amplitude of the target response voltage is outlined in thick
solid lines in the Figure.

30 The moment when the exciting pulse is turned off is defined as time $t = 0$, and the monitoring of the sample response signal commences some time after $t = 0$, during
35 the ring down period. The ring down time, t_r , of the target material is defined, in the notation of the Figure, as the instant when the peak-to-peak target response voltage is 10% of V_r . As used herein, the term
"ring down time" means the time interval during which the amplitude of response from the ribbon is reduced to

about 10% of that amplitude extant when an exciting pulse applied to the ribbon is terminated, such time interval commencing at the instant of termination of the exciting pulse.

5 The ring down time, t_r , is approximately a linear function of the ribbon length, L ; the longer the ribbon, the longer is the ring down time. Without being bound by any theory, it is believed that the increase in t_r with increasing L is associated with the lowering of the
10 mechanical resonance frequency in longer ribbons. The same amount of energy takes longer to dissipate at lower frequencies.

 The magnitude of the response voltage sensed by a receiver is dependent on how that receiver is disposed
15 within the system. For example, a receiver in a system requiring the insertion of an identification card into a slot will perceive a magnitude for V_r that is different from that perceived by a receiver in a system designed for employment at the exit doors of a department store,
20 even though identical target materials are used in both systems.

 There are no requirements on the magnitude of V_r as far as the choice of target material is concerned. It is, however, understood that the value for V_r should be
25 such that the response voltage is of sufficient strength to be detected by the receiver at the instant, during the ring down period, when the receiver "listens" to the target material. Henceforth, for the reasons detailed immediately above, no further reference to V_r will be
30 made in the description of this invention.

 Table I lists the values for t_r obtained from various metallic glass alloys that are outside the scope of this invention but which happen to lie within the scope of compositions claimed in the '489 and '490
35 patents. With the exception of the last named alloy, the ring down times for the alloys in this Table are short. This last named alloy is prone to the difficulties associated

with the casting of alloys with high molybdenum contents.

TABLE I

5 Ring down times, t_r , obtained from ribbons of metallic glass alloys that are outside the scope of this invention. Representative compositions from a variety of metallic glass systems have been listed. Except as
10 noted, these ribbons have mechanical resonance frequencies, f_r , in the range from about 55 kHz to 60 kHz.

15	Composition (at.%)	t_r (ms)
	$\text{Fe}_{78}\text{B}_{13}\text{Si}_9$	1.2
	$\text{Fe}_{81}\text{B}_{13.5}\text{Si}_{3.5}\text{C}_2$	1.5
20	$\text{Fe}_{66}\text{Co}_{18}\text{B}_{15}\text{Si}_1$	1.0
	$\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$	5.2 (*)
	$\text{Fe}_{42}\text{Ni}_{38}\text{Mo}_2\text{B}_{18}$	1.8
	$\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_4\text{B}_{18}$	4.3

25 (*) Ribbon with f_r of about 22 kHz.

It has been found that the combination of the
30 specific elements in the alloys of this invention is necessary for the attainment of long ring down times. Short ring down times result from metallic glass alloys that have any one of these elements absent from their composition. Table II lists the ring down times
35 obtained from representative metallic glass alloys wherein both Si and C are absent, and Table III contains a similar list derived from alloys with no C. The alloys in these Tables are outside the scope of this

invention, and the undesirable ring down times obtained from these alloys are self evident from these Tables.

It is understood from the Tables II and III that the alloy $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_4\text{B}_{18}$ is unique in terms of its long ring down time. A lowering of the molybdenum content to make the alloy more economical to produce invariably compromises the ring down time. It will be further understood from the Tables I to III that the long ring down times obtained in the alloys of this invention, with the stated combination of the specific elements,

TABLE II

Ring down times, t_r , obtained from ribbons of metallic glass alloys containing Fe, Ni, Mo, and B, but no Si or C. Except as noted, these ribbons have mechanical resonance frequencies, f_r , in the range from about 21 kHz to about 23 kHz.

20

Composition (at.%)

 t_r (ms)

25

 $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_3\text{B}_{19}$

6.0

 $\text{Fe}_{40}\text{Ni}_{39}\text{Mo}_3\text{B}_{18}$

6.0

 $\text{Fe}_{41}\text{Ni}_{38}\text{Mo}_3\text{B}_{18}$

1.8 (*)

(*) Ribbon with f_r of about 58 kHz.

30

35

TABLE III

Ring down times, t_r , obtained from ribbons of metallic glass alloys containing Fe, Ni, Mo, B, and Si, but no C. These ribbons have mechanical resonances in the range of frequencies from about 21 kHz to about 23 kHz.

Composition (at.%)	t_r (ms)
$\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_4\text{B}_{17}\text{Si}_1$	2.6
$\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_4\text{B}_{16}\text{Si}_2$	5.5

are much longer than the ring down times of previous target materials.

The following examples are presented to provide a more complete understanding of the invention. The specific techniques, conditions and reported data set forth to illustrate the principles and practice of the invention are exemplary and should not be construed as limiting the scope of the invention. All alloy compositions described in the examples are nominal compositions.

EXAMPLESExample 1: Fe-Ni-Mo-B-Si-C metallic glasses1. Sample Preparation

Glassy metal alloys in the Fe-Ni-Mo-B-Si-C family, designated as samples no. 1 to 13 in Table IV, were rapidly quenched from the melt following the techniques taught by Narasimhan in U.S. Patent No. 4,142,571, the disclosure of which is hereby incorporated by reference thereto. All casts were made in a vacuum chamber, using

25 to 100 g melts. The resulting ribbons, typically 25 to 30 μm thick and about 6 mm wide, were determined to be free of significant crystallinity by x-ray diffractometry using Cu-K_α radiation and differential scanning calorimetry. Each of the alloys was at least 70% glassy and, in many instances, the alloys were more than 90% glassy. Ribbons of these glassy metal alloys were strong, shiny, hard, and ductile.

10 2. Characterization of response as resonance targets

Ribbon samples, cut to about 38 mm in length, were used for the characterization of ring down times in the various alloys. This ribbon length is appropriate to a mechanical resonance frequency ranging from about 55 kHz to about 60 kHz in these alloys. The biasing dc field and the driving ac field were obtained from two solenoids that were coaxially configured. The biasing solenoid, about 0.38 m in length, had a turn density of about 3400 turns/m, and the driving solenoid was about 0.3 m long with a turn density of about 1440 turns/m. The sample was placed on the axis of these solenoids, at about the middle of their length. The sample response was sensed through a pick-up coil comprising between about 100 and 120 turns of wire wound closely around the sample and covering the entire ribbon length. The sample response (pick-up signal) and the driving ac signal were simultaneously monitored on an oscilloscope screen.

An initial estimation of the resonance frequencies of these as-cast ribbon samples was made by fixing the dc biasing field at about 440 A/m and scanning the frequency of a driving ac field of a constant amplitude of about 8 A/m. Peaks in the respective response signals identified the resonance frequencies, which were found to range from about 55 to kHz to about 60 kHz.

Following the above procedure, for any given sample, a pulse was sent through the exciting solenoid, which pulse contained a counted number of waves at the

resonance frequency determined earlier as appropriate for the sample. The number of waves, or, equivalently, the duration of the pulse, was adjusted to be sufficient to ensure that the sample response had reached a stable value. Adjustments to the driving frequency, and to the biasing field strength, were also made, when necessary, to obtain a maximum sample response signal. Peak sample responses were obtained with the biasing field ranging from about 400 A/m to about 600 A/m, the driving frequency ranging from about 56 kHz to about 58 kHz, and the exciting pulse comprising between about 80 and 100 waves.

The traces on the oscilloscope screen were as schematically illustrated in the Figure. As described above, the ring down time was determined as the time required for the sample response amplitude to reduce to 10% of the amplitude at the instant the exciting pulse was turned off. Table IV below lists the ring down times obtained from these 38 mm long as-cast metallic glass ribbons.

25

30

35

TABLE IV

Ring down times, t_r , obtained from various Fe-Ni-Mo-B-Si-C metallic glasses belonging to this invention. Mechanical resonance frequencies range from about 55 kHz to about 60 kHz.

		Composition						t_r (ms)
No.		Fe	- Ni	- Mo	- B	- Si	- C	
10	1 at.%	40	- 38	- 2	- 19	- 0.5	- 0.5	5.3
	wt.%	45.8	- 45.7	- 3.9	- 4.2	- 0.3	- 0.1	
	2 at.%	40	- 38	- 2	- 18.5	- 1	- 0.5	7.5
	wt.%	45.7	- 45.6	- 3.9	- 4.1	- 0.6	- 0.1	
15	3 at.%	40	- 38	- 3	- 18	- 0.5	- 0.5	4.7
	wt.%	45.0	- 44.9	- 5.8	- 3.9	- 0.3	- 0.1	
	4 at.%	40	- 38	- 1.5	- 18.5	- 1	- 1	6.3
	wt.%	46.1	- 46.0	- 3.0	- 4.1	- 0.6	- 0.2	
	5 at.%	40	- 38	- 1.5	- 18	- 1.5	- 1	5.0
	wt.%	46.0	- 45.9	- 3.0	- 4.0	- 0.9	- 0.2	
20	6 at.%	40	- 38	- 2	- 18.5	- 0.5	- 1	6.3
	wt.%	45.8	- 45.7	- 3.9	- 4.1	- 0.3	- 0.2	
	7 at.%	40	- 38	- 2	- 18	- 1	- 1	5.0
	wt.%	45.7	- 45.6	- 3.9	- 4.0	- 0.6	- 0.2	
25	8 at.%	40	- 38	- 2	- 17.5	- 1.5	- 1	5.0
	wt.%	45.6	- 45.5	- 3.9	- 3.9	- 0.9	- 0.2	
	9 at.%	40	- 38	- 2.5	- 17.5	- 1	- 1	5.7
	wt.%	45.3	- 45.2	- 4.9	- 3.8	- 0.6	- 0.2	
	10 at.%	40	- 38	- 3	- 17	- 1	- 1	6.5
	wt.%	44.9	- 44.8	- 5.8	- 3.7	- 0.6	- 0.2	
30	11 at.%	40	- 38	- 1	- 18	- 1.5	- 1.5	5.1
	wt.%	46.4	- 46.3	- 2.0	- 4.0	- 0.9	- 0.4	
	12 at.%	40	- 38	- 1.5	- 18	- 1	- 1.5	4.2
	wt.%	46.1	- 46.0	- 3.0	- 4.0	- 0.6	- 0.4	
35	13 at.%	40	- 38	- 2	- 17	- 1.5	- 1.5	5.5
	wt.%	45.6	- 45.5	- 3.9	- 3.8	- 0.9	- 0.4	

Each of the alloys listed in Table IV showed good castability and had a ring down time of at least about 4.2 ms, which is relatively long as compared with alloys outside the scope of the invention. Of the alloys set forth in Table IV, those selected from the group consisting of sample Nos. 2, 4, 6, 7 and 10, having a ring down time of at least about 5 ms, are preferred.

Annealing of metallic glasses improves their soft ferromagnetic characteristics. Consequently, the ring-down times of the metallic glasses of this invention are improved if these glassy alloys are annealed.

Ribbons of selected alloys from the above Table were subject to simple stress relief anneals, i.e., low temperature anneals in the absence of externally imposed magnetic fields. The anneal temperature ranged between about 473 K and 573 K, and the anneal time ranged between about 15 min. and 60 min. Ring down times from these annealed ribbons were found to be longer than in the corresponding as-cast ribbons. The extent of increase was dependent on the chemical composition of the metallic glass and on the anneal conditions for a given alloy. Other anneal conditions which may optimize the magnetomechanical coupling effects available in a metallic glass alloy ribbon, such as those including the presence of external fields applied along the ribbon width, can be employed to improve the resonance target response of the alloys of this invention.

Example 2: Fe-Ni-Cr-B-Si-C metallic glasses

Glassy metal alloys in the Fe-Ni-Cr-B-Si-C system were prepared and characterized as detailed under Example 1. The ring down times obtained from representative alloys in this family of metallic glasses are listed in Table V.

TABLE V

Ring down times, t_r , obtained from various Fe-Ni-Cr-B-Si-C metallic glasses belonging to this invention. Mechanical resonance frequencies range from about 55 kHz to about 60 kHz.

No.	Composition							t_r (ms)
		Fe	- Ni	- Cr	- B	- Si	- C	
10	1 at.%	40	- 38	- 3	- 18	- 1	- 0	3.8
	wt.%	46.1	- 46.1	- 3.2	- 4.0	- 0.6	- 0	
	2 at.%	40	- 38	- 2	- 18	- 2	- 0	4.1
	wt.%	46.4	- 46.3	- 2.2	- 4.0	- 1.2	- 0	
15	3 at.%	40	- 38	- 0	- 18	- 2	- 2	4.1
	wt.%	47.1	- 47.1	- 0	- 4.1	- 1.2	- 0.5	

Example 3

Numerous casts were made of the alloy $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_2\text{B}_{18}\text{Si}_1\text{C}_1$, which belongs to this invention, and of the alloy $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_4\text{B}_{18}$, which is outside the scope of this invention, following the procedures detailed under Example 1. Uniformity in width, and a lack of holes and kinks were used as the criteria for selection of "good" 38 mm long ribbons, usable as target material. About 10 to 15 such ribbons could be derived from a typical cast of the alloy belonging to this invention, whereas the alloy outside the scope of this invention yielded only 4 to 8 such ribbons from a typical cast.

The above stated criteria are good indicators of the potential yield from a large scale cast of metallic glass ribbon. Kinks develop in the ribbons cast in a vacuum chamber when the ribbon, that is still hot, contacts the walls of the vacuum chamber. Under otherwise similar casting conditions, an alloy that is more efficiently quenched into ribbon will show fewer kinks along the length of the ribbon. Similarly, it is

understood that a lack of uniformity in width, and the presence of holes in the cast ribbon, evidence reduced castability of the alloy.

Having thus described the invention in rather full
5 detail, it will be understood that such detail need not
be strictly adhered to but that further changes and
modifications may suggest themselves to one skilled in
the art, all falling within the scope of the invention
as defined by the subjoined claims.

10

15

20

25

30

35

What is claimed is:

1. A magnetic metallic glass alloy that is at least about 70% glassy, having a composition described by the formula $\text{Fe}_a\text{Ni}_b\text{M}_c\text{B}_d\text{Si}_e\text{C}_f$, where M is one of molybdenum and chromium, "a" - "f" are in atom percent,
5 "a" ranges from about 39 to about 41, "b" ranges from about 41, "b" ranges from about 37 to about 39, "c" ranges from 0 to about 3, "d" ranges from about 17 to about 19, and "e" and "f" range from 0 to about 2, with the provisos that (i) only one of "c", "e" and "f" can be zero, (ii) "e"
10 cannot be zero if "f" is not zero, and (iii) "f" can be zero only when M is Cr.
2. An alloy as recited by claim 1, having the form of a strip that exhibits mechanical resonance in a range of frequencies from about 55 kHz to about 60 kHz, and
15 having a ring down time of at least about 3 ms.
3. The magnetic alloy of claim 2, wherein said ring down time is greater than about 5 ms.
4. The magnetic alloy of claim 2, wherein "e" or "f" ranges between about 0.5 and about 2.
- 20 5. The magnetic alloy of claim 2, wherein each of "e" and "f" ranges between about 0.5 and about 1.
6. In an article surveillance system adapted to detect a signal produced by mechanical resonance of a target within an applied magnetic field, the improvement
25 wherein said target comprises at least one strip of ferromagnetic material that is at least about 70% glassy, and has a composition described by the formula $\text{Fe}_a\text{Ni}_b\text{M}_c\text{B}_d\text{Si}_e\text{C}_f$, where M is one of molybdenum and chromium, "a" - "f" are in atom percent, "a" ranges
30 from about 39 to about 41, "b" ranges from about 41, "b" ranges from about 37 to about 39, "c" ranges from 0 to about 3, "d" ranges from about 17 to about 19, and "e" and "f" range from 0 to about 2, with the provisos that (i) only one of "c", "e" and "f" can be zero, (ii) "e"
35 cannot be zero if "f" is not zero, and (iii) "f" can be zero only when M is Cr.

-20-

7. An article surveillance system as recited by claim 9, wherein said strip is selected from the group consisting of ribbon, wire and sheet.

8. An article surveillance system as recited by claim 9, wherein said strip exhibits mechanical resonance in a range of frequencies from about 55 kHz to about 60 kHz, and has a ring down time of at least about 3 ms.

9. An article surveillance system as recited by claim 8, wherein "e" and "f" range between about 0.5 and about 1.

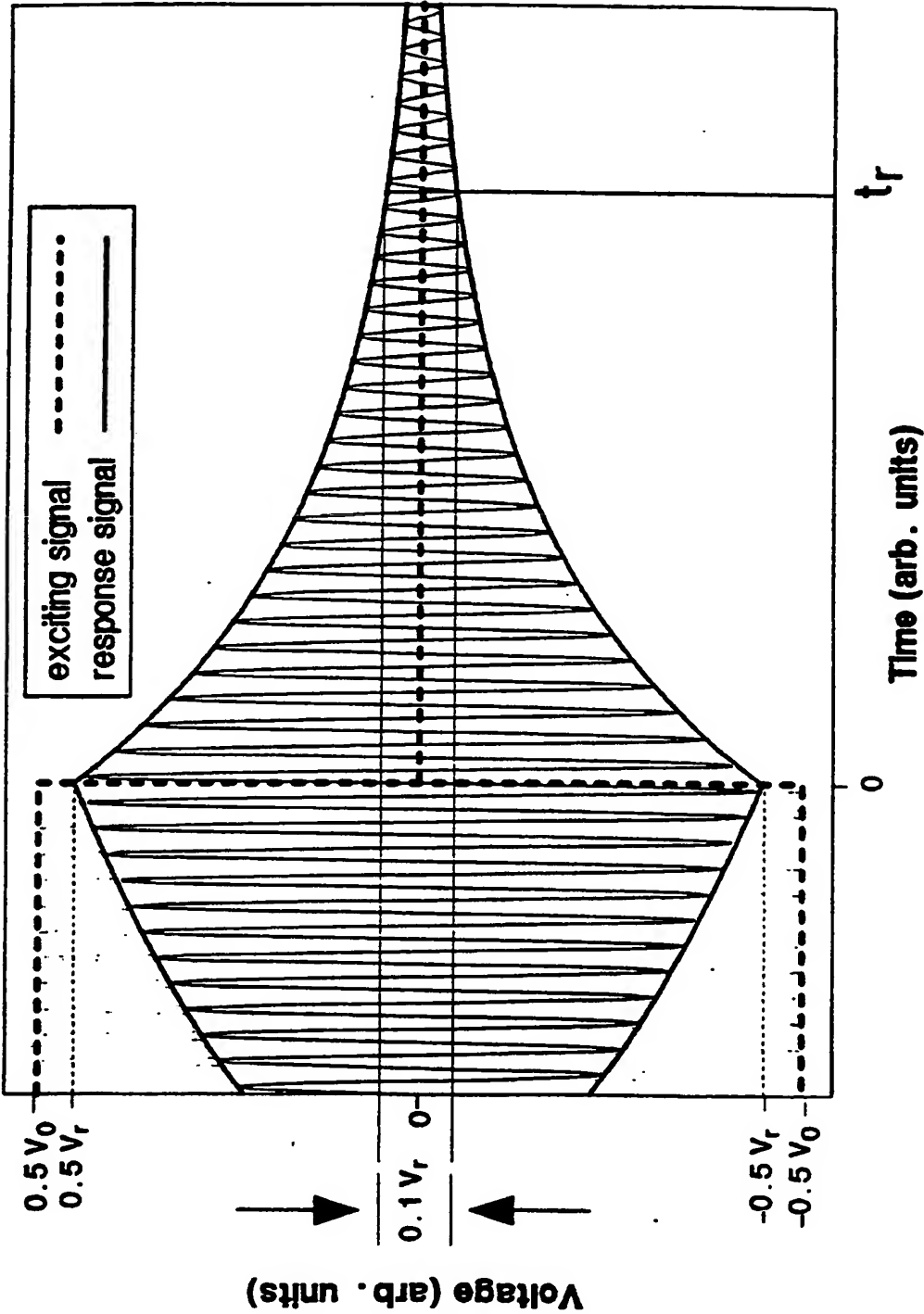
10. An article surveillance system as recited by claim 6, wherein said strip has a composition selected from the group consisting of $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_2\text{B}_{18}\text{Si}_1\text{C}_1$, $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_{1.5}\text{B}_{18.5}\text{Si}_1\text{C}_1$, $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_2\text{B}_{18.5}\text{Si}_1\text{C}_{0.5}$, $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_2\text{B}_{18.5}\text{Si}_{0.5}\text{C}_1$ and $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_3\text{B}_{17}\text{Si}_1\text{C}_1$.

20

25

30

35



INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 89/03513

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : H 01 F 1/153, G 08 G 13/24																	
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border-right: 1px solid black; padding: 5px;">IPC⁵</td> <td style="padding: 5px;">H 01 F, G 08 G</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁵	H 01 F, G 08 G											
Classification System	Classification Symbols																
IPC ⁵	H 01 F, G 08 G																
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category ¹⁰</th> <th style="width: 70%; border-bottom: 1px solid black;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%; border-bottom: 1px solid black;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 4510489 (P.M. ANDERSON et al.) 9 April 1985, see claims 1-4 (cited in the application) --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1,6,7</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 4510490 (P.M. ANDERSON et al.) 9 April 1985, see claims 1-4 (cited in the application) --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1,6,7</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A, 0096551 (UNITIKA LTD) 21 December 1983 --</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A, 0042525 (TOKYO SHIBAURA DENKI K.K.) 30 December 1981 -----</td> <td></td> </tr> </table>			Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	US, A, 4510489 (P.M. ANDERSON et al.) 9 April 1985, see claims 1-4 (cited in the application) --	1,6,7	A	US, A, 4510490 (P.M. ANDERSON et al.) 9 April 1985, see claims 1-4 (cited in the application) --	1,6,7	A	EP, A, 0096551 (UNITIKA LTD) 21 December 1983 --		A	EP, A, 0042525 (TOKYO SHIBAURA DENKI K.K.) 30 December 1981 -----	
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³															
A	US, A, 4510489 (P.M. ANDERSON et al.) 9 April 1985, see claims 1-4 (cited in the application) --	1,6,7															
A	US, A, 4510490 (P.M. ANDERSON et al.) 9 April 1985, see claims 1-4 (cited in the application) --	1,6,7															
A	EP, A, 0096551 (UNITIKA LTD) 21 December 1983 --																
A	EP, A, 0042525 (TOKYO SHIBAURA DENKI K.K.) 30 December 1981 -----																
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁴ Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"G" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search <div style="text-align: center;">7th November 1989</div> </td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center;">06.12.89</div> </td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;"> International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="border-bottom: 1px solid black; padding: 5px;"> Signature of Authorized Officer <div style="text-align: right;"> <div style="text-align: right; margin-top: 5px;">T.K. WILLIS</div> </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center;">7th November 1989</div>	Date of Mailing of this International Search Report <div style="text-align: center;">06.12.89</div>	International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: right;"> <div style="text-align: right; margin-top: 5px;">T.K. WILLIS</div> </div>											
Date of the Actual Completion of the International Search <div style="text-align: center;">7th November 1989</div>	Date of Mailing of this International Search Report <div style="text-align: center;">06.12.89</div>																
International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: right;"> <div style="text-align: right; margin-top: 5px;">T.K. WILLIS</div> </div>																

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 8903513

SA 30742

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 28/11/89. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4510489	09-04-85	AU-B- 565131	03-09-87
		AU-A- 1294883	03-11-83
		CA-A- 1200871	18-02-86
		EP-A, B 0093281	09-11-83
		JP-A- 58192197	09-11-83
		US-A- 4510490	09-04-85

US-A- 4510490	09-04-85	US-A- 4510489	09-04-85
		AU-B- 560069	26-03-87
		AU-A- 1294983	08-12-83
		CA-A- 1200872	18-02-86
		EP-A, B 0096182	21-12-83
		JP-A- 58219677	21-12-83
		AU-B- 565131	03-09-87
		AU-A- 1294883	03-11-83
		CA-A- 1200871	18-02-86
		EP-A, B 0093281	09-11-83
		JP-A- 58192197	09-11-83

EP-A- 0096551	21-12-83	JP-A- 58213857	12-12-83
		CA-A- 1223139	23-06-87
		US-A- 4473401	25-09-84

EP-A- 0042525	30-12-81	JP-A- 57013146	23-01-82
		CA-A- 1182308	12-02-85
		US-A- 4385932	31-05-83

EPO FORM 1007

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.